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(54) Title: INK JET PRINTABLE MICROPOROUS FILM (57) Abstract A durable ink jet printable medium comprising a microporous ethylene vinyl alcohol copolymer film. The microporous film has a pore diameter sufficient to absorb pigment particles from a pigment-based ink and a pore volume sufficient to absorb all of the ink directed towards the film. The ink jet printable medium can include a pressure sensitive adhesive on a major surface thereof to form a durable label for use with ink jet printers. Also disclosed is a method of ink jet printing an image onto such a recording medium.		

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INK JET PRINTABLE MICROPOROUS FILM

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TECHNICAL FIELD

The present invention relates generally to an ink jet printable microporous film, and more particularly to a durable ink jet printable microporous film, pressure sensitive labels and labelstock incorporating such film, and a method of printing such film.

10

BACKGROUND OF THE INVENTION

Ink jet printing is a well-known and commonly used means of imparting an image onto a substrate. Two common ink jet printing methods are continuous ink jet printing and drop-on-demand ink jet printing. These methods have in common the ability to direct a stream of droplets from a reservoir of ink through a nozzle and onto a substrate to form a desired image.

In drop-on-demand ink jet printing, the droplets of ink are produced only when needed. Drop-on-demand ink jet printing itself includes two common methods of creating the droplets. In piezoelectric drop-on-demand printing, a piezoelectric crystal produces a pressure on the reservoir of ink to expel a droplet from the nozzle. In thermal drop-on-demand printing, an electrical input to a tiny resistor causes a minute quantity of the ink in the reservoir to boil and form a bubble. As the bubble expands, a drop of ink is forced out of the nozzle towards the substrate. Thermal ink jet printing is also referred to as bubble jet printing. In continuous ink jet printing, a continuous stream of ink droplets is generated through a nozzle under constant pressure. Electric charges are applied to the particular droplets that are to form the image. Charged deflection plates direct the charged droplets to the desired location on the substrate. Drops that are not charged are collected in a gutter and recycled. For a general discussion of ink jet printing techniques, see Levy and Biscos, Nonimpact Electronic Printing, pp. 34-39 (InterQuest, 1993); A.J. Rogers, Ink Jet Takes Off, Byte, October 1991, pp. 163-168; and Craig K. Harmon and Russ Adams, Reading Between the Lines, pp. 75-77 (Helmets Publishing, Inc. 3d ed., 1984).

Thermal ink jet printers are discussed in greater detail in U.S. Patent No. 5,420,625, "Ink Supply System for a Thermal Ink-Jet Printer," (Dietl et al.). Dietl et al. discusses certain known ink jet printer arrangements such as those in which the print head comprises one or more ink filled channels communicating with a relatively small ink supply chamber, or manifold, at one end and having an opening at the opposite end, referred to as a nozzle, such as disclosed in U.S. Pat. No. 4,463,359. A thermal energy generator, usually a resistor, is located in each of the channels at a predetermined distance from the nozzles. The resistors are individually addressed with a current pulse to momentarily vaporize the ink and form a bubble which expels an ink droplet. As the bubble grows, the ink bulges from the nozzle and is contained by the surface tension of the ink as a meniscus. As the bubble begins to collapse, the ink still in the channel between the nozzle and bubble starts to move towards the collapsing bubble, causing a volumetric contraction of the ink at the nozzle and resulting in the separation of the bulging ink as a droplet. The acceleration of the ink out of the nozzle while the bubble is growing provides the momentum and velocity of the droplet in a substantially straight line direction towards a recording medium, such as paper. The current pulses to the heater are shaped to prevent the meniscus from breaking up and receding too far into the channel after each droplet is expelled. Various embodiments of linear arrays of thermal ink jet devices are known, such as those having staggered linear arrays attached to the top and bottom of a heat sinking substrate and those having different colored inks for multiple colored printing. A common type of print head is known as a "sideshooter." Sideshooters are so named because the ink droplets are emitted through the channel at a right angle relative to the heating element. U.S. Pat. No. 4,774,530 describes such a construction in greater detail. U.S. Pat. No. 4,638,337 describes a sideshooter in which the sudden release of vaporized ink known as blowout is prevented by disposing the heater in a recess. Sideshooter print heads are generally present in ink jet printers available from Canon Kabushiki Kaisha of Tokyo, Japan and Xerox Corporation of Stamford, Connecticut. Another common type of print head is known as a "roof shooter." Such print heads are generally present

in ink jet printers available commercially from Hewlett-Packard Company of Palo Alto, California.

Thermal drop-on-demand ink jet printing is also further discussed in U.S. Patent No. 5,422,664, "Method and Apparatus for Maintaining Constant Drop Size Mass In Thermal Ink Jet Printers," (Stephany).

Continuous ink jet printing is further discussed in U.S. Patent No. 4,929,966, "Continuous Ink Jet Printer with a Gravity Drain, Catcher System," (Sexton et al.).

10 Sexton et al. explains that in continuous ink jet printers, streams of uniformly spaced ink drops are created by imposing predetermined vibrations upon liquid ink filaments issuing from an orifice plate. The filaments are formed by supplying ink under pressure to a print head cavity that is in communication with the orifice plate. Information is imparted to the droplet streams by selective non-charging or charging and deflection of

15 droplets. A portion of the droplets pass to the recording medium but there are a substantial number of non-printing droplets that are intercepted by a catcher device and returned for recirculation. Often the print head cavity has an outlet other than the orifice plate (e.g. to facilitate dynamic pressure control within the cavity at start-up), and the apparatus ink supply system also recirculates such ink flow. In many

20 applications a variety of other fluid couplings to the ink reservoir may be used. For example, a common practice in continuous ink jet printers is to provide a vacuum system that is coupled to the interior of the ink supply reservoir. The reduced pressure in the reservoir is used to return ink from a print head outlet line and/or from a home station where start-up and cleaning operations can occur. In one embodiment

25 disclosed in Sexton et al., the ink jet printer includes an improved ink return system for a continuous ink jet printer of the kind having a droplet generator for directing streams of ink droplets along a print path, an ink supply reservoir and means for supplying ink from the reservoir to the droplet generator. The return system includes: (i) a catcher having a catcher inlet located laterally adjacent the droplet print path for receiving non-

30 print droplets, a catcher outlet and a discharge passage constructed and located to

slope downwardly from the catcher inlet to the catcher outlet; and (ii) a return conduit that slopes continuously downwardly from the catcher outlet to the ink reservoir.

Multicolor continuous ink jet printers are discussed in U.S. Patent No. 5 4,875,055. "Simplified Multicolor Fluid System for Continuous Ink Jet," (McCann et al.). McCann et al. explains that in a continuous ink jet printer system, ink is supplied under pressure to the orifice cavity of a resonator body and ejects as continuous streams from an orifice plate aimed toward a print zone. The resonator body is vibrated to cause the ink streams to break up into uniformly sized and shaped droplets. 10 A charge plate subsystem is located proximate the stream break-up point and droplets are selectively charged if intended to be non-printing ones. The charged, non-printing drops are deflected to a catcher subassembly which routes them back to the main ink supply. Uncharged drops pass on to the print zone. U.S. Pat. Nos. 4,591,875; 4,607,261 and 4,614,948, describe continuous ink jet printers of the kind wherein a 15 print head can traverse to and from the home station and along an operative print path. The '875 and '261 patents disclose fluid handling systems wherein ink reservoirs are constructed as readily replaceable cartridges that cooperate with fluid conduits of the printer in an easily connectable and disconnectable fashion.

20 It is seen from the above, that the construction and operation of drop-on-demand and continuous ink jet printers is well known in the art, and need not be discussed in greater detail herein.

Certain applications require durable labels. Such durable labels can be used to 25 display the following types of information: bar codes; information about chemical contents; price; property identification; inventory identification; model number and serial number of an article (so-called "rating plates"); warranty information; and wiring diagrams. It may be desirable to place these types of information in a durable way on the following: appliances; communications equipment; computers, including peripheral 30 equipment and accessories; electronics; industrial products and parts; retail products; automobiles; and goods or packages being transported or shipped. Many different

printing techniques are available for printing labels and label stock. These techniques include thermal transfer, ink jet, electrophotographic, and flexographic. It is desirable that the printing technique chosen for the above applications conveniently and inexpensively provides durable labels, with the ability to print variable information, that is information which changes from label to label. While ink jet printing is particularly well suited for printing labels with variable information and for providing multicolor printing, it has heretofore been impossible to ink jet print a durable label without the need for an overlamine or overcoat.

10 The above-noted need for durability in adhesive labels for certain applications is evident from the issuance of a standard from American National Standard Institute ("ANSI") and Underwriters Laboratories ("UL") concerning the durability of marking and labeling systems. This standard and test methods are set forth in ANSI/UL 969-1991, "Standard for Marking and Labeling Systems". This ANSI/UL standard applies to adhesive labels for use as nameplates or markers bearing information, instructions, or identification, and to unprinted labelstock used by label makers to produce labels. While the present invention is not limited to labels and labelstock which meet the requirements of ANSI/UL standard 969-1991, the standard provides a useful framework for comparing the durability of the labels and labelstock of the present invention with known printable materials. The 969 standard defines, among other things, required adherence of the label to a test surface, legibility of the image, and resistance to scraping. These indicators of durability are to be measured after exposure for a specified time to various environments, such as standard atmosphere, water, elevated temperature, and various oils and solvents.

25 For a printed label to be durable, there must be adequate durability of the printing substrate, the adhesive, and the image. The durability of the printing substrate is determined by its chemical composition which affects solubility and its resistance to mechanical wear, abrasion, and/or distortion. Durability of the adhesive is determined by its chemical composition. The durability of the image is determined by the lightfastness and waterfastness of the colorant in the ink, and the degree to which the

ink is absorbed into the substrate and below the top surface of the substrate, such as into the pores and below the surface of a microporous polymeric film substrate.

Ink jet printers generally can use one of two common types of ink: dye-based
5 inks and pigment-based inks. With dye-based ink, the color of the ink is imparted by a dye which is soluble in the fluid carrier. The major fluid carrier is typically a blend of water and glycol. Such dye-based inks are relatively inexpensive and easy to process, and are suitable for use in low cost applications in which long term durability is not a concern. In pigment-based inks, the color is imparted by particles which are dispersed,
10 rather than dissolved, in a fluid carrier. Most pigments are insoluble in organic solvents and water and can be chosen for lightfastness. In contrast, most dyes are organic and tend to be less stable when subjected to heat, sunlight, and/or chemicals. Therefore, pigment-based inks are more suitable for durable label applications, such as those discussed above. Accordingly, there is a need for a printable material which can
15 be used with ink jet printing techniques and pigment-based inks to produce a durable label.

Many ink jet printable substrates are known in the art. And while each may have its own utility, no known ink jet printable substrates are capable of conveniently
20 and inexpensively providing a durable label.

Papers commercialized for ink jet printing have special coatings, often containing silica. These coating are porous because of the high loading of filler. However, the paper substrate itself is not durable. Also, many coated paper substrates
25 are not sufficiently absorptive so as to be non-smearing immediately after printing.

A possible way to achieve image durability is to use a film overlamine or an overprint varnish. A film overlamine consists of a plastic film with a pressure sensitive adhesive which is placed over the image and label to be protected. An
30 overprint varnish is in liquid form or paste form and is coated over the image and label to be protected using a suitable press such as a flexographic press. For most end users,

these are undesirable ways of achieving a durable label because of the increased expense and complexity of obtaining additional equipment and supplies and because of the increased process steps required.

5 A single layer, microporous, high molecular weight polyethylene film, highly filled with silica is available from PPG Industries, Inc., of Pittsburgh, Pennsylvania, and is known commercially as TESLIN™ Synthetic Printing Sheet. Such film is purported to be ink jet printable, and to be water, chemical, and abrasion resistant. However, such films have been observed to require an undesirably long time for black pigmented
10 ink to dry, and have been observed to show degradation of image quality in response to abrasion, particularly after exposure to certain fluids. Additionally, this film is not available commercially in calipers less than 0.18 mm (0.007 in), which can cause difficulty in feeding the sheet through curved paths in a printer. This is aggravated when a pressure sensitive adhesive and liner is present, increasing the overall thickness.
15 Similar film constructions are also disclosed in U.S. Patent Nos. 4,861,644 and 5,196,262.

Thus, there is seen to be a need for a durable ink jet printable material suitable for use as an adhesive label or labelstock, and which can be conveniently manufactured
20 and printed without the need for an additional layer or treatment after the film is manufactured or printed.

SUMMARY OF THE INVENTION

One aspect of the present invention presents a method of ink jet printing an
25 image onto a recording medium. The method comprises the steps of: a) directing a plurality of droplets of ink towards the recording medium, wherein the recording material comprises a microporous ethylene vinyl alcohol copolymer film; b) contacting the ink droplets on a first surface of the microporous ethylene vinyl alcohol copolymer film so as to impart a desired image on the first surface; and c) absorbing the ink into
30 the pores of the microporous ethylene vinyl alcohol copolymer film. In a preferred embodiment of the invention, the film has a thickness of from 0.0015 to 0.006 inches.

In another preferred aspect of the above method, ink comprises a plurality of pigment particles suspended in a fluid carrier, and step c) comprises absorbing the particles into the pores of the microporous ethylene vinyl alcohol copolymer film. In
5 another preferred embodiment of this method, the film has a maximum limiting pore diameter sufficient to absorb the pigment particles. In another preferred embodiment, the film has a maximum limiting pore diameter of at least 0.1 micrometers. In a further preferred embodiment, the film has a maximum limiting pore diameter of at least 0.4 micrometers.

10

In yet further preferred aspects of the above method, the microporous ethylene vinyl alcohol copolymer film has a sufficient pore volume to absorb all of the ink directed towards the film, or the film has a pore volume of at least 25 nL/mm², or the film has a pore volume of from 25 to 300 nL/mm².

15

The above method can optionally comprise the further step of d) subsequent to step c), providing an adhesive on the second surface of the microporous ethylene vinyl alcohol copolymer film. In one preferred embodiment, the adhesive is a pressure sensitive adhesive. Another embodiment includes the further step of e) providing a
20 release liner on the exposed surface of the pressure sensitive adhesive.

The above method can optionally include the further step of a') prior to step a), providing an adhesive on the second surface of the microporous ethylene vinyl alcohol copolymer film. In one embodiment of this method, the adhesive is a pressure sensitive
25 adhesive and step a') further includes providing a release liner on the exposed surface of the pressure sensitive adhesive.

In one aspect of the above method, the image is dry to the touch within one minute after printing. In another aspect, the image is dry to the touch substantially
30 immediately after printing.

The present invention also presents a method of ink jet printing an image onto a recording medium comprising the steps of: a) directing a plurality of droplets of ink towards the recording medium, wherein the ink comprises a plurality of pigment particles suspended in a fluid carrier, and wherein the recording material comprises a microporous ethylene vinyl alcohol copolymer film, the film having a pore volume sufficiently large to absorb the ink and a maximum limiting pore diameter sufficiently large to absorb the particles; b) contacting the ink droplets on a first surface of the microporous ethylene vinyl alcohol copolymer film so as to impart a desired image on the first surface; and c) absorbing the fluid carrier and pigment particles into the pores of the microporous ethylene vinyl alcohol copolymer film. In one preferred embodiment of this method, the microporous ethylene vinyl alcohol copolymer film has a pore volume of at least 25 nL/mm² and a maximum limiting pore diameter of at least 0.1 micrometers.

Another aspect of the present invention presents an ink jet printable medium. The ink jet printable medium comprises a microporous ethylene vinyl alcohol copolymer film having a first major surface and a second major surface. In one preferred embodiment, the microporous film has a pore volume of at least 25 nL/mm². In another preferred embodiment, the microporous film has a pore volume of from 25 to 300 nL/mm².

In a further preferred embodiment of the ink jet printable medium, the microporous film has a maximum limiting pore diameter of at least 0.1 micrometers. In still a further preferred embodiment, the microporous film has a maximum limiting pore diameter of at least 0.4 micrometers.

In yet another preferred embodiment of the ink jet printable medium, the microporous film is from 0.0015 to 0.006 inches thick.

The ink jet printable medium can optionally include a layer of adhesive provided on the second major surface of the film. In one preferred embodiment,

adhesive is a pressure sensitive adhesive. The medium can include an optional release liner provided on the exposed surface of the pressure sensitive adhesive.

The present invention also presents an ink jet printable medium, comprising a
5 microporous ethylene vinyl alcohol copolymer film having a first major surface and a second major surface, the film having a pore volume of at least 25 nL/mm², a maximum limiting pore diameter of at least 0.1 micrometers, and a thickness of from 0.0015 to 0.006 inches; a layer of pressure sensitive adhesive provided on the second major surface of the film; and a release liner provided on the exposed surface of the
10 layer of pressure sensitive adhesive. In one preferred embodiment of this ink jet printable medium, the microporous ethylene vinyl alcohol copolymer film comprises a pore volume of from 25 to 300 nL/mm² and a maximum limiting pore diameter of at least 0.4 micrometers.

15 BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be further explained with reference to the appended Figures, wherein like structure is referred to by like numerals throughout the several views, and wherein:

Figure 1 is a partially schematic cross section of a drop-on-demand ink jet head
20 and microporous film according to the present invention;

Figure 2 is a partially schematic cross section of a continuous ink jet print head and microporous film according to the present invention;

Figure 3 is a cross sectional view of an adhesive labelstock according to the present invention;

25 Figure 4 is an enlarged view of the label portion of the labelstock of Figure 3; and

Figure 5 is a partially schematic illustration of a method and apparatus for forming the microporous film of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 is a partially schematic cross sectional view of drop-on-demand ink jet print head 10. Print head 10 includes reservoir 12 and nozzle 14. The reservoir 12 and nozzle 14 together form a cavity for storing a quantity of ink 30. At the forward end of the nozzle 14 is orifice 16, for allowing droplets 34 of ink 30 to exit the print head 10 in a manner described in greater detail below. Ink is supplied to reservoir 12 through inlet 20. Print head 10 also includes drive means 18. Drive means 18 typically comprises a resistive heater when the print head 10 is used in a thermal drop-on-demand ink jet printer, also sometimes known as a bubble jet printer. Drive means 18 comprises a piezoelectric crystal when the print head 10 is used in a piezoelectric drop-on-demand ink jet printer. Control input 22 (illustrated schematically) provides the appropriate input to drive means 18 to cause the print head 10 to expel a droplet 34 in the direction of microporous film 70.

Operation of drop-on-demand print head 10 is as follows. When the print head 10 is used in a thermal drop-on-demand ink jet printer, drive means 18 comprises a thermal energy generator, usually a resistor. The resistor 18 is individually addressed with a current pulse by control input 22 from a suitable control means (not illustrated) to momentarily vaporize the ink 30 adjacent the resistor 18 and thereby form a bubble adjacent the resistor. Formation of the bubble expels an ink droplet precursor 32 through orifice 16 of nozzle 14. As the bubble grows, the droplet precursor 32 bulges from the nozzle 14 and is contained by the surface tension of the ink as a meniscus. When the current pulse to resistor 18 is removed, the resistor begins to cool and the bubble adjacent the resistor begins to collapse. As the bubble adjacent resistor 18 begins to collapse, the ink 30 still in the reservoir 12 between the nozzle and bubble starts to move towards the collapsing bubble, causing a volumetric contraction of the ink 30 at the nozzle 14 and resulting in the separation of the bulging ink 32 as a droplet 34. The acceleration of the ink 30 out of the nozzle 14 while the bubble is growing provides the momentum and velocity of the droplet 34 in a substantially straight line direction towards the microporous film 70 which serves as the recording medium. The print head 10 and microporous film 70 can be translated relative to one another as is

well known in the art to direct the droplets 34 to the desired location on microporous film 70 to create the desired image.

When drop-on-demand print head 10 comprises a piezoelectric print head, the
5 operation is much the same as with the thermal process described above, with the following differences. Drive means 18 comprises a piezoelectric crystal. An electrical signal is applied to the crystal 18 by control input 22, causing a small dimensional change in the crystal 18 that creates a pump-like action. This dimensional change forces droplet precursor 32 to emerge from orifice 16 of nozzle 14. When the
10 electrical signal is removed and the crystal 18 relaxes, the droplet 34 separates from the ink 30 and is propelled toward the microporous film 70 as described above.

Figure 2 illustrates a partially schematic cross section of a continuous ink jet print head 40. Print head 40 includes a nozzle 42 having an orifice 44. Pump 48
15 (shown schematically) provides ink 30 under pressure into inlet 46 of print head 40 via supply line 58. Pressure from pump 48 continuously ejects ink 30 from orifice 44 of nozzle 42. The print head 40 acts as (or can be in communication with) a resonator body. The resonator body is vibrated with a piezoelectric crystal, for example, to cause the stream of ink 30 to break up into uniformly sized and shaped droplets 34. A
20 charge plate subsystem including charging plates 60a and 60b is located proximate the stream break-up point and selectively charges droplets 34a that are intended to print an image on the film 70. The uncharged, non-printing droplets 34b are deflected to a catcher subassembly which routes them back to the main ink supply. The catcher subassembly includes gutter 52 for catching the unused droplets and supply line 54 for
25 delivering the unused ink to ink supply 50. This unused ink is then provided to pump 48 via supply line 56, to be recirculated into print head 40. The charge imparted on droplets 34a by charging plates 60a and 60b is varied so as to vary the deflection caused to such droplets by control plates 62a and 62b. The varying deflection directs droplets 34a to the desired location on microporous film 70 to create the desired
30 image. Print head 40 may also be translated relative to microporous film 70 to direct the droplets 34a as desired.

Commercially available ink jet printers and pigment-based inks suitable for use with the present invention include the Hewlett-Packard DeskJet™ and DeskWriter™ printer models 600C and 660C, available with ink jet cartridge HP51629A; printer models 850C and 855C available with ink jet cartridge HP51645A; printer model 1200C available with ink jet cartridge HP51640A; printer model 1600C/CM available with ink jet cartridge HP51645A; and the Design Jet™ printer model 650C available with ink jet cartridges HP51640A and HP51626A, all available commercially from Hewlett-Packard Company of Palo Alto, California, although the present invention is not thereby limited. For example, the microporous film of the present invention may be used advantageously with other ink jet printers, ink jet inks, such as dye-based inks, and with other printing methods.

Figure 3 illustrates a cross section of a labelstock 80 incorporating microporous film 70. Film 70 includes first surface 72 for receiving the ink 30 as described above, and second surface 74 opposite the first surface 72. Adhesive layer 76 is provided on second surface of film 70. Optional release liner 78 can be provided on adhesive 76 as is well known in the art, and is preferred when the adhesive is a pressure sensitive adhesive.

20

Adhesives useful in the preparation of an adhesive coated labelstock according to the present invention include both pressure sensitive and non-pressure sensitive adhesives such as hot melt and curable adhesives. Pressure sensitive adhesives are normally tacky at room temperature and can be adhered to a surface by application of, at most, light finger pressure, while non-pressure sensitive adhesives include solvent, heat, or radiation activated adhesive systems. Pressure sensitive adhesives are a preferred class of adhesives for use in the present invention. Examples of adhesives useful in the invention include those based on general compositions of polyacrylate; polyvinyl ether; diene-containing rubber such as natural rubber, polyisoprene, and polyisobutylene; polychloroprene; butyl rubber; butadiene-acrylonitrile polymer; thermoplastic elastomer; block copolymers such as styrene-isoprene and styrene-

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isoprene-styrene block copolymers, ethylene-propylene-diene polymers, and styrene-butadiene polymer; poly-alpha-olefin; amorphous polyolefin; silicone; ethylene-containing copolymer such as ethylene vinyl acetate, ethylacrylate, and ethyl methacrylate; polyurethane; polyamide; epoxy; polyvinylpyrrolidone and
5 vinylpyrrolidone copolymers; polyesters; and mixtures of the above. Additionally, the adhesives can contain additives such as tackifiers, plasticizers, fillers, antioxidants, stabilizers, pigments, diffusing particles, curatives, and solvents.

A general description of useful pressure sensitive adhesives may be found in
10 Encyclopedia of Polymer Science and Engineering, Vol. 13, Wiley-Interscience Publishers (New York, 1988). Additional description of useful pressure sensitive adhesives may be found in Encyclopedia of Polymer Science and Technology, Vol. 1, Interscience Publishers (New York, 1964).

15 Other pressure sensitive adhesives useful in the invention are described in the patent literature. Examples of these patents include Re 24,906 (Ulrich), U.S. Patent No. 3,389,827 (Abercrombie et al.), at Col. 4-Col. 5, U.S. Patent No. 4,080,348 (Korpman), U.S. Patent No. 4,136,071 (Korpman), U.S. Patent No. 4,181,752 (Martens et al.), U.S. Patent No. 4,792,584 (Shiraki et al.), U.S. Patent No. 4,883,179 (Young et al.),
20 and U.S. Patent No. 4,952,650 (Young et al.). Commercially available adhesives are also useful in the invention. Examples include those adhesives available from 3M Company, St. Paul, MN; H.B. Fuller Company, St. Paul, MN; Century Adhesives Corporation, Columbus, OH; National Starch and Chemical Corporation, Bridgewater, NJ; Rohm and Haas Company, Philadelphia, PA; and Air Products and Chemicals,
25 Inc., Allentown, PA.

In one preferred embodiment, the labelstock 80 comprising microporous film 70, adhesive 76, and release liner 78 is fed through the ink jet printer for imaging. It is, of course, also within the scope of the present invention to feed microporous film 70
30 itself through the ink jet printer for imaging. The imaged film 70 could then be converted into labelstock or label 80 for application to a desired surface. Alternatively,

the imaged film 70 could be used as is, for example installed in a suitable holder or frame, or taped to a surface.

Microporous film 70 comprises a microporous ethylene-vinyl alcohol
5 copolymer (EVOH). The copolymer preferably has an internal structure of a
multiplicity of spaced, randomly dispersed, non-uniform shaped particles of ethylene-
vinyl alcohol copolymer. Preferably, the particles are joined together by fibrils. The
EVOH film can be prepared by (a) melt blending a mixture of ethylene-vinyl alcohol
10 copolymer and a compatible polymer or compound in which the copolymer will
dissolve to form a solution at the melting temperature of the copolymer, but will phase
separate on cooling at or below the crystallization temperature of the ethylene-vinyl
alcohol copolymer, (b) forming a film of the melt blended mixture; (c) cooling the
film to a temperature to cause phase separation to occur between the compatible
15 copolymer or compound and the ethylene-vinyl alcohol copolymer, thereby providing a
film which is an aggregate of a first phase comprising particles of ethylene-vinyl
alcohol copolymer in a second phase of the compatible polymer or compound with
adjacent ethylene-vinyl alcohol copolymer particles being distinct but having a plurality
of zones of continuity; and (d) i) collecting the film which has adjacent ethylene-vinyl
20 alcohol copolymer particles which form a network of interconnected micropores
therebetween, or ii) extracting the compatible polymer or compound with water and
stretching the film in at least one direction while wet to further separate adjacent
ethylene-vinyl alcohol copolymer particles from one another and to permanently
attenuate the ethylene-vinyl alcohol copolymer in the zones of continuity to form fibrils
therebetween and drying, or iii) extracting the compatible polymer or compound with
25 an organic solvent.

When the compatible polymer or compound is removed from the film by
extraction with an organic solvent, the film may optionally be stretched in a heated
condition before or after removal of the compatible polymer or compound to further
30 separate adjacent ethylene-vinyl alcohol copolymer particles from one another and to
permanently attenuate the ethylene-vinyl alcohol copolymer in the zones of continuity

to form fibrils therebetween. Preferably, the compatible polymer or compound is a polyhydric alcohol.

The thus-formed EVOH microporous film is inherently hydrophilic, can have
5 porosity in the range of about 10 to 75 percent, and possesses good tensile properties.

The formed film, before removal of the compatible polymer or compound and stretching, is generally transparent or translucent, and comprises an aggregate of a first phase of particles of EVOH in a second phase of the compatible polymer or
10 compound. The particles may be described as spherulites and aggregates of spherulites of the polymer, with the compatible polymer or compound occupying the space between particles. Adjacent particles of copolymer are distinct, but they have a plurality of zones of continuity. That is, the copolymer particles are generally surrounded or coated by the compatible polymer or compound, but not completely.
15 There are areas of contact between adjacent copolymer particles where there is a continuum of copolymer from one particle to the next adjacent particle in such zones of continuity.

On stretching, the copolymer particles are pulled apart, permanently
20 attenuating the copolymer in zones of continuity, thereby forming the fibrils and creating a network of interconnected micropores. Such permanent attenuation also renders the film permanently translucent or opaque. Also on stretching, if the compatible polymer or compound is not removed, the compatible polymer or compound remains coated on or surrounds, at least partially, the surfaces of the
25 resultant EVOH particles. The degree of coating, of course, depends upon the affinity of the compatible polymer or compound for the surface of the copolymer particle, whether the compatible polymer or compound is a liquid or solid, whether stretching dislodges or disrupts the coating, and upon other relevant factors. The particles are usually at least partially coated after stretching. Substantially all of the particles appear
30 to be connected by fibrils.

The size of the micropores is easily controlled by varying the degree of stretching, the amount of compatible polymer or compound employed, melt-quench conditions, compatible polymer or compound removal, and heat stabilization procedures. For the most part, the fibrils do not appear to be broken by stretching, but
5 they are permanently stretched beyond their elastic limit so that they do not elastically recover to their original position when the stretching force is released. As used herein, "stretching" means such stretching beyond the elastic limit so as to introduce permanent set or elongation of the film.

10 The ethylene-vinyl alcohol copolymers may be random, block or graft copolymers preferably having an ethylene unit content of about 20 to 90 mol percent, more preferably about 25 to 50 mol percent. The degree of saponification of the copolymer is preferably at least about 80 mol percent, more preferably at least about 95 mol percent, based on the vinyl alcohol units in the copolymer. An insufficient
15 degree of saponification may result in insufficient wet mechanical properties for some purposes. Preferably, the number average molecular weight of the ethylene-vinyl alcohol copolymer is at least about 2000 g/mol, more preferably at least about 20,000 g/mol, most preferably at least about 40,000 g/mol with higher molecular weight copolymers frequently exhibiting better processing and strength characteristics.

20

The ethylene and vinyl alcohol monomers may be copolymerized with another copolymerizable monomer such as methacrylic acid, vinyl chloride, methyl methacrylate, acrylonitrile and vinyl pyrrolidone to form a terpolymer with the amount of copolymerizable monomer being less than about 15 mol percent. Where a
25 functional group is present as a result of the copolymerizable monomer in the terpolymer, the functional group can serve to provide sites for crosslinking. Crosslinkages may be introduced into the ethylene-vinyl alcohol copolymers or terpolymers by irradiation such as, for example, ultraviolet, electron beam or gamma irradiation. Crosslinkages may also be introduced into the ethylene-vinyl alcohol
30 copolymers before or after membrane formation by treatment with an inorganic crosslinking agent such as a boron compound or an organic crosslinking agent such as

a diisocyanate or a dialdehyde. Such crosslinking agents also may be included in the melt blend as long as the phase separation is not adversely affected. Useful ethylene-vinyl alcohol copolymers also include those in which the functional hydroxyl groups of vinyl alcohol units are partially crosslinked with an aldehyde such as formaldehyde, acetaldehyde, butyraldehyde or benzaldehyde but preferably to an extent of not more than about 30 mol percent.

Compounds suitable for blending with the ethylene-vinyl alcohol copolymer to make the microporous materials are liquids or solids at room temperature, in which the copolymer will dissolve to form a solution at the melting temperature of the copolymer, but will phase separate on cooling at or below the crystallization temperature of the copolymer. Preferably, these compounds have a boiling point at atmospheric pressure at least as high as the melting temperature of the ethylene-vinyl alcohol copolymer. However, compounds having lower boiling points may be used in those instances where superatmospheric pressure may be employed to elevate the boiling point of the compound to a temperature at least as high as the melting temperature of the crystallizable polymer. Generally, suitable compounds have a solubility parameter and a hydrogen bonding parameter within a few units of the values of these same parameters for the crystallizable polymer.

20

Suitable compounds for blending with the ethylene-vinyl alcohol copolymers include, for example, polyhydric alcohols such as polyethylene glycol, polypropylene glycol, ethylene glycol, triethylene glycol, and glycerin. Preferably, the polyhydric alcohol has a number average molecular weight below about 600 g/mol to provide sufficient compatibility with the ethylene-vinyl alcohol copolymer.

25

A particular combination of copolymer and compatible polymer or compound may include more than one copolymer, i.e., a blend of two or more copolymers and/or more than one compatible polymer or compound. Optionally, if desired, the copolymer may include blended therein certain conventional additive materials, which materials should be limited in quantity so as not to interfere with the formation of the

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microporous material and so as not to result in unwanted exuding of the additive. Such additives may include, for example, antistatic materials, antioxidants, dyes, plasticizers, elastomers, ultraviolet light absorbers, and the like. When used, the amount of such conventional additive is typically less than about 10% of the weight of the copolymer component, and preferably less than about 2% by weight.

The melt blend preferably comprises from about 30 to about 80 parts by weight of the ethylene-vinyl alcohol copolymer and about 20 to about 70 parts by weight of the compatible polymer or compound, more preferably from about 40 to about 70 parts by weight of the ethylene-vinyl alcohol copolymer and about 30 to about 60 parts by weight of the compatible polymer or compound. The ethylene-vinyl alcohol copolymer and the compatible polymer or compound are preferably heated to at least the melting temperature of the melt blend and preferably to a temperature in the range of about 10 to 100°C above the melt temperature of the melt blend for ease of handling of the melt.

The EVOH films useful in the present invention may be prepared by casting a shaped film such as a sheet or layer from the melt blend comprising the ethylene-vinyl alcohol copolymer and the compatible polymer or compound. Depending upon the particular copolymer employed, the film is cooled in a quench bath at an appropriate temperature, preferably at least about 60°C below the equilibrium melting point of the pure copolymer, to provide a proper cooling rate. For example, for ethylene-vinyl alcohol copolymer melt blend having an equilibrium melting point of 175°C, a cooling temperature between about 40°C and about 120°C or more is employed. Some minor degree of experimentation may be required to identify the appropriate temperature range which produces optimum phase separation for a particular copolymer/compatible polymer or compound system, this being well within the capability of those skilled in the art once apprised of the present disclosure.

The attainment of the EVOH microporous films is dependent upon the rate of cooling. During cooling, heat is removed from the melt blend until the crystallization

temperature of the ethylene-vinyl alcohol copolymer in the melt blended mixture is reached, and solidification and phase separation of the copolymer can begin. Cooling temperatures greater than about 160°C below the equilibrium melting point of the pure copolymer may cause too rapid quenching of the melt blend and can result in single
5 phase form, which, although strong and transparent, are substantially incapable of being rendered uniformly microporous by stretching.

Reference will now be made to the apparatus of Figure 5 in order to illustrate one preferred method for practicing the present invention. The ethylene-vinyl alcohol
10 copolymer is introduced into the hopper 112 of an extruder apparatus 110. The compatible polymer or compound is fed by a suitable feeding device 113 into the extruder 110 via a port 111 in the extruder wall intermediate the hopper 112 and an extruder exit 117. The extruder preferably has at least three zones, 114, 115, and 116 which are respectively heated at decreasing temperatures towards the extruder exit
15 117. A slot die 119, having a slit gap of about 25 to about 1000 micrometers, is positioned after the extruder. It is also preferable to utilize a suitable mixing device such as a static mixer 118 between the extruder exit 117 and the slot die 119. In passing through the extruder and, where used, the static mixer, the mixture of copolymer and compatible polymer or compound is heated to a temperature at or at
20 least about 10°C above the melting temperature of the melt blend, but below the thermal degradation temperature of the copolymer, and is mixed to form a melt blend that is extruded through the slot die 119 as a layer 125 onto a quench wheel 120 maintained at a suitable temperature below the crystallization temperature of the ethylene-vinyl alcohol copolymer.

25 The cooled film may then be led from the quench wheel 120 to a compatible polymer or compound removal bath 121 containing water or another solvent capable of dissolving the compatible polymer or compound but not the ethylene-vinyl alcohol copolymer, if removal of the compatible polymer or compound is desired. The film,
30 when water is used as the extraction bath, preferably is then directed to a machine-direction stretching device 122 and a transverse direction stretching device 123, and

then to a take-up roller 124 for winding into a roll. Where a solvent other than water is used to remove the compatible polymer or compound, the film may be dried prior to stretching and then stretched in a heated condition, e.g., from about 70°C to 140°C. Stretching in two directions as done by the apparatus of Figure 5 is, of course,
5 optional.

A further method of forming a membrane material from the blended melt includes casting the extruded melt onto a patterned chill roll to provide areas where the blend does not contact the chill roll to provide a membrane of substantially uniform
10 thickness having a patterned surface, the patterned surface providing substantially skinless areas having high microporosity and skinned areas of reduced microporosity. Such a method is described in U.S. Pat. No. 5,120,594 (Mrozinski). Alternatively, the membrane material may be cast onto a wheel coated with the compatible polymer or compound used to form the melt blend. The membrane material can then be extracted
15 and oriented, i.e., stretched, as described above.

The porosity of the microporous films can be increased by stretching, typically with an increase in length (elongation) of about 10%. Stretching to provide a total area increase of about 10% to about 1200% is generally useful. The actual amount of
20 stretching required will depend upon the particular composition of the film and the degree of porosity desired. Stretching may be provided by any suitable device which can provide stretching in at least one direction, and may provide stretching both in that direction and in the transverse direction. Stretching should be uniform to obtain uniform and controlled porosity.

25

The microporous sheet materials of the present invention are preferably dimensionally stabilized according to conventional, well known techniques, such as by heating the stretched sheet, while it is restrained, at a heat stabilizing temperature.

30

If the microporous film of the invention is dried but not annealed, i.e., subjected to a heat treatment, it is dimensionally stable as long as the film is kept in equilibrium

by constant temperature and humidity. Dimensional stability under conditions of changing temperature and humidity can be improved with higher annealing temperatures. Shrinkage when exposed to heat or water is a feature which can make the microporous film useful for moisture indicating or for forcing another compound from the pores of the film after exposure. For printing applications, it is preferable to avoid curling caused by mismatched dimensional changes of the microporous film and optional release liner under heat and humidity. This can be accomplished by selecting the release liner and microporous film to have substantially equal expansivity properties.

10

The films of the present invention generally possess sufficient tensile strength for subsequent handling, depending upon the tensile strength of the ethylene-vinyl alcohol copolymer employed, the zones of continuity, the extent of stretching, and the various process conditions.

15

The compatible polymer or compound may be removed from the microporous sheet to provide a unique microporous sheet material formed only of the ethylene-vinyl alcohol copolymeric material. Removal of the polyhydric alcohol may be accomplished by extraction, volatilization, or any other convenient method. The preferred extraction solvents include water and organic solvents such as, for example, isopropyl alcohol, ethanol, methanol, n-butanol, hydrochlorofluorocarbons, acetone, methyl ethyl ketone and 1,1,1-trichloroethane.

20

In describing various embodiments of the microporous EVOH film 70, the following terms will be used. Porosity is indicated by a value expressed as percent porosity, which is determined by dividing the measured density of the microporous EVOH film by the bulk density of EVOH, subtracting that ratio from 1, and multiplying by 100. The term "percent porosity" is used throughout, including the claims, as just described. Bubble point is an indication of the maximum limiting pore diameter ("MLPD") of the pores of the microporous EVOH film, and is measured in accordance with ASTM F 316-86, "Standard Test Methods for Pore Size

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Characteristics of Membrane Filters by Bubble Point and Mean Flow Pore Test." This test determines the minimum pressure required to blow the first continuous bubbles through the microporous film after prewetting the film, the bubbles being detectable by their rise through a layer of liquid. This pressure is used to calculate the flow-limiting diameter of the pores. The term "maximum limiting pore diameter," and its abbreviation MLPD, is used throughout, including the claims, as determined by the just-described standard test method. The term "pore volume" as used throughout, including the claims, is the volume of pores in the film per unit of projected surface area of the film. It is determined by multiplying the percent porosity by the thickness of the film (in micrometers) and dividing by 100 to get a pore volume indicated in nanoliters per square millimeter (nL/mm²). Throughout the application, including the claims, wherever thickness of the microporous film is reported or used to calculate another characteristic, it is determined by measuring the combined thickness of four stacked layers of film in three locations, determining the average stack thickness of the three locations, and dividing by four.

When using a pigment-based ink to image the microporous EVOH film 70, it is necessary that the pigment particles are carried into the pores of the film and below the top surface 72. This makes the particles resistant to being rubbed off the surface of the film, or from being easily lifted off and carried away from the film by liquids. The pore diameter must be large enough to accept the pigment particles. Additionally, the fluid carrier of the pigment particles must wet the EVOH polymer to allow the carrier and pigment particles to flow into the pores. There must also be sufficient pore volume to imbibe the volume of ink jetted onto the film.

In considering the pore volume available for absorption of the ink, reference is made to Figure 4. Figure 4 illustrates a cross section of the label comprising microporous film 70 having adhesive 76 provided on second surface 74. Dimension (a) illustrates the total thickness of the film 70. Dimension (b) indicates the thickness to which adhesive 76 is absorbed into film 70 through surface 74. Resulting thickness (c) is therefore the available film thickness in which the ink can be absorbed.

Dimension (b) can be calculated from data obtained from measurement techniques such as mercury porosimetry. Generally, thickness (b) will be a function of the porosity of the film 70, the composition of the adhesive 76, and the time, pressure, and temperature at which the labelstock 80 is stored prior to printing. Pore volume of the film itself can be calculated for the full thickness (a) of the film. However, where an adhesive is absorbed partly into the thickness of the film, the available pore volume is that amount of pore volume for thickness (c) of the film. For quick or immediate drying of the image, it is desirable to have enough available pore volume to absorb the amount of ink deposited onto the surface 72 of the film. However, as the available pore volume exceeds the minimum amount necessary to absorb the ink, the ink will be absorbed deeper into the film away from surface 72 which decreases the optical density of the image. Accordingly, it is desirable to select the available pore volume to achieve a desired combination of drying time and optical density.

For use of the film of the present invention with currently available desk top ink jet printers, a pore volume of at least 25 nL/mm^2 is desirable for the film to absorb substantially all of the ink directed to the surface of the film. This can be obtained by selecting the desired combination of thickness, MLPD, and percent porosity. However, for some printers or film applications, it may be desirable to have a smaller or larger pore volume. For example, as the drop volume of the particular ink jet printer chosen increases, the pore volume for the film preferably should be increased. Additionally, to be able to absorb the pigment particles in currently available ink jet inks, it is desirable to have a MLPD of at least 0.1 micrometers. Again, this may vary depending upon the ink selected and the application of the film. One preferred film of the present invention has an MLPD of approximately 0.5 micrometers, a pore volume of approximately 40 nL/mm^2 , and a thickness of approximately 100 micrometers (0.004 inches).

The Washburn equation in linear velocity form describes the effects of pore radius (r), ink liquid surface tension (σ) and viscosity (μ), dynamic advancing contact angle (θ) between liquid and capillary wall, and the length of the capillary already filled

(x) on the velocity of penetration (v):

$$v = (r)(\sigma)(\cos(\theta)) / 4(\mu)(x)$$

For a positive velocity v, $\cos(\theta)$ must be positive. Therefore, the advancing contact angle, measured for the particular ink of interest, must be between 0° and 90°, meaning
5 that the ink fluid must wet the polymer for absorption of the ink fluid carrier into the pores to occur. Penetration into the pores must occur if the ink is to be non-smearing. The smaller the contact angle, θ , the faster the penetration and the shorter the dry time. Fast penetration is desirable so that printed substrates can be conveniently handled and stacked soon after printing.

10

The operation of the present invention will be further described with regard to the following detailed examples. These examples are offered to further illustrate the various specific and preferred embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within
15 the scope of the present invention.

Examples 1-13

The effect of MLPD and pore volume of the microporous EVOH film on the drying time of the ink is demonstrated with respect to Examples 1-13. It is expected
20 that the pore diameter must be sufficiently large to allow the pigment particles to flow with the ink fluid carrier below the surface of the microporous film, and that the pore volume must be sufficiently large to contain the quantity of ink deposited on the film. Examples 1-13 had a maximum limiting pore diameter ("MLPD") ranging from 1.54 micrometers down to less than 0.15 micrometers, as determined by the bubble point
25 test described above. Also reported with respect to Examples 1-13 is the pore volume reported in units of nanoliters per projected square millimeter of film. These two characteristics are varied during the manufacturing process described above by varying the diluents used, the ratio of the diluents to one another, the concentration of the diluent relative to the EVOH polymer, and by varying processing conditions such as
30 extruder screw speed, cast film thickness, quench temperature, and orientation ratios. A test image in the form of a pattern of a number of letter E's, 12 point size, was

printed on the sample films with a Hewlett-Packard DeskJet™ 1200C printer with HP51640A black pigment-based ink. Drying time of the images was determined by placing the printed sample on a hard surface and rubbing the printed image firmly 10 times back and forth with a tissue immediately after printing. If the image smeared, an

5 unrubbed portion of the image is again tested thirty seconds after printing, one minute after printing, five minutes after printing, and then ten minutes after printing. The optical density of the image is also reported for examples 1-13 in Table 1. After the image was allowed to dry for 24 hours, reflected optical density was measured with a

10 Macbeth™ TR-924 Status Densitometer available commercially from Macbeth Process Measurements, a division of Kollmorgen Corporation, of Newburgh, New York.

TABLE 1

Example	MLPD (μ)	Pore Volume (nL/mm ²)	Film Thickness (μ)	Ink Dry Time	Image Optical Density
1	1.54	82.1	140	Immediate	1.06
2	1.36	46.2	84	Immediate	1.02
3	0.97	53.0	114	Immediate	1.02
4	0.77	74.1	117	Immediate	1.02
5	0.76	44.1	109	Immediate	1.09
6	0.65	31.3	104	>10 min	1.17
7	0.62	55.9	150	Immediate	0.82
8	0.54	40.2	107	Immediate	1.08
9	0.47	32.3	109	Immediate	1.01
10	0.42	34.3	79	>10 min	1.18
11	0.24	36.0	81	>10 min	1.67
12	0.19	27.1	61	>10 min	1.96
13	<0.15	16.0	41	>10 min	--

15 It can be seen from the results reported in Table 1, that for the volume of ink deposited and the particle size used in the specific ink in the Examples, that MLPD and pore volume should be kept sufficiently large to allow for absorption of the pigment-based ink into the microporous film. The volume of ink jetted onto the surface by the

ink jet printer used with Examples 1-13 is calculated to be 25 nL/mm², based on a 45 picoliter (pL) drop size and 236x236 dots per centimeter (600x600 dots per inch). As the measured MLPD of Examples 1-13 drops below 0.47 micrometers, the drying time was in excess of 10 minutes, demonstrating that to attain immediate drying time, the pore diameter must be sufficiently large to absorb the pigment particles. As the measured pore volume of Examples 1-13 drops below 32 nL/mm², the drying time was in excess of 10 minutes, demonstrating that to attain immediate drying time, the pore volume of the microporous film must be sufficiently high to absorb all of the ink deposited on the surface of the film.

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Examples 14-16

Example 14 was prepared with an extrusion mix of 66% Eval F100B resin from Eval Company of America and 34% polyethylene glycol (PEG-200) from Dow Chemical Co. The film was formed with a slip gap sheeting die and drop cast onto a pattern casting wheel. Next, the polyethylene glycol diluent was exchanged with water. The film was then length oriented and width oriented. Lastly, the film was heated to drive out the water and anneal the film. Characteristics of the washed and dried microporous EVOH film are reported in Table 2. The casting wheel side of the film of Example 14 was laminated towards Scotch™ 9458 adhesive. A number of individual samples for testing were then converted from the film of Example 14. Examples 15 and 16 were prepared with an extrusion mix of 63% Eval F100B resin, 27.75% PEG-200, and 9.25% glycol. The film was formed as described with respect to Example 14. The characteristics of the films of Examples 15 and 16 are reported in Table 2. For the films of Examples 15 and 16, a paper with a silicone release layer was adhesive-coated with a tackified acrylic pressure-sensitive adhesive using a fluid-bearing die with a dry coating weight target of 1.76 milligrams per cm² (4.2 grains per 24 in²). The coated liner was moisturized before facestock was laminated in. These rolls were then slit to 216 mm (8.5 in) wide for manual cutting to 216 by 279 mm (8.5 by 11 in) sheets. The samples of Examples 14 and 15 were then fed through a Hewlett-Packard DeskJet™ 1200C printer and printed with a black "E" pattern using HP51640A pigmented black ink. The image dried immediately, and the letters were

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observed to be very crisp, with sharp edges. The black image appeared to be "washed-out" somewhat (i.e. low optical density) and there was some backgrounding, a common occurrence with ink jet. The film of Example 14 appeared to be very brittle and may be suitable for use as fragile film or destructible labelstock. The samples of Example 16 were then fed through a Hewlett-Packard DeskJet™ 660C printer and printed with a black "E" pattern using HP51629A pigmented black ink. The image was checked one minute after printing and was found to be dry and of good image quality.

Also reported in Table 2 are the average tensile strength at break, average percent elongation at break, and average tensile energy to break of Examples 15-16. Such measurements are taken in accordance with ASTM D 882-91, "Standard Test Methods for Tensile Properties of Thin Plastic Sheeting," test method A, using a 0.1 mm per mm-minute strain rate and 2.54 cm (1 in) wide samples. These mechanical properties of the microporous film are currently believed to provide a general indication of the processability of the film material itself. The film should be strong enough to withstand web tensions when making the film and when making labelstock. It should have characteristics which allow it to be slit, die cut, and/or sheeted. The film should be strong enough so that as weed or matrix it may be conveniently stripped without breaking. It has been observed that the mechanical properties of the microporous films generally decrease with increasing percent porosity and decreasing thickness. Accordingly, the percent porosity and thickness should be selected to provide the desired combination of pore volume to achieve adequate drying time and mechanical properties to achieve film processability.

Abrasion resistance samples of the films of Examples 14-16 were tested by using a Taber™ Abraser Model 503 with Calibrase™ CS-10 wheels. The test was performed under a 500 gram load for 100 cycles on films which were adhered to a cardboard backing plate. Abrasion did not degrade the image. Interestingly, the abrasion appeared to collapse the microporous film somewhat, thereby increasing the optical transmission of the film and increasing the optical density of the image.

Heat resistance of a sample of the film of Example 14 was determined by adhering the film to an aluminum test panel and subjecting the film to 180°C (356°F) for 11 days. The image remained legible, although the film turned very brown and shrunk in both directions.

Printed samples of the labels of Examples 14-16 were adhered to test panels and subjected to various immersion tests. Effects of immersion are reported both before and after rubbing the samples ten times back and forth with a cheesecloth under firm hand pressure. Immersion results for durability of the image and film on samples prepared from Examples 14-16 are reported in Table 3. Samples prepared in accordance with Example 15 were subjected to tests described in ANSI/UL 969-1991, with the exception that the carbon-arc weatherometer cycle was performed with a 120 minute cycle: 102 minutes of light only, 18 minutes of light and water spray. Test methods are summarized in Table 4A; test results are reported in Table 4B. These results show that labels prepared in accordance with Example 15 meet the requirements of ANSI/UL 969-1991.

20

TABLE 2

	Example 14	Example 15	Example 16
MLPD (μ)	0.84	0.54	0.59
Film Thickness (μ)	97	107	109
Bulk Density (g/cc)	0.494	0.742	0.725
Porosity (%)	58.0	37.7	39.1
Pore Volume (nL/mm ²)	56.0	40.2	42.7
Avg. Tensile Strength at Break (megapascals) MD/CD ⁽¹⁾	--	24.5/17.7	26.8/20.7
Avg. Percent Elongation at Break (%), MD/CD	--	26.6/41.5	24.6/42.9
Average Tensile Energy to Break (megajoules/m ²), MD/CD	--	5.7/6.1	5.7/7.4

⁽¹⁾ MD = machine direction of film; CD = crossweb direction of film.

TABLE 3

IMMERSION CONDITIONS	Example 14		Example 15		Example 16	
	Before Rubbing	After Rubbing	Before Rubbing	After Rubbing	Before Rubbing	After Rubbing
Deionized Water, 4 hours @ RT ⁽¹⁾	No Effect	No Effect	--	--	No Effect	No Effect
pH 4.0 Solution ⁽²⁾ 4 hours @ RT	No Effect	No Effect	No Effect	No Effect	No Effect	No Effect
pH 10.0 Solution ⁽³⁾ 4 hours @ RT	No Effect	No Effect	No Effect	No Effect	No Effect	No Effect
Detergent Solution ⁽⁴⁾ 4 hours @ RT	No Effect	No Effect	No Effect	No Effect	No Effect	No Effect
Isopropanol, 4 hours @ RT	No Effect	No Effect	No Effect	No Effect	No Effect	No Effect
DOT 3 Brake Fluid, 4 hours @ RT	No Effect	No Effect	No Effect	No Effect	No Effect	No Effect
Ethylene Glycol and Water (50/50 by volume), 4 hours @ 95°C (203°F)	Image optical density increased	No Effect	--	--	--	--
	Film dissolved; no image left	Not Applicable	--	--	--	--

⁽¹⁾ RT = Room Temperature (72°F, 22°C)⁽²⁾ 50 ml of 0.1 molar potassium hydrogen phthalate plus 0.1 ml of 0.1 molar HCl⁽³⁾ 50 ml of 0.025 molar sodium borate plus 18.3 ml of 0.1 molar NaOH⁽⁴⁾ 1% solution by volume AlconoxTM wetting agent and detergent from Alconox, Inc., New York, NY

TABLE 4A

Test Method	Examination	Legibility Test	Defacement Test	Adhesion Test
	Visual	Rub printing with thumb or finger back and forth ten times with a downward force of approx. 4 pounds	Scrape back and forth ten times across printing and edges with a blade using a downward force of approx. 2 pounds	90° - 2 in/min peel rate
Required Result	Shall adhere without any significant curling or loosening around the perimeter, or other indication of loss of adhesion such as wrinkles or bubbles; shall not excessively craze or shrink; printing shall be legible	Printing shall be legible	Shall remain in place and shall not be torn or otherwise damaged	Minimum of 0.5 lb/in width or sample shows good adhesion when removed by hand

TABLE 4B

Exposure	Visual Examination	Legibility Test	Defacement Test	Adhesion * (lb. per in.)
Standard Atmosphere 72 hours	Good adherence; no shrinkage; printing legible	Good	Good	PP: 2.1 PC: 2.5 ABS: 2.5 SS: 2.5
Water Immersion 48 hours at Room Temperature	Good adherence; slight shrinkage (1.5%, 1.0%); printing legible	Good	Good	PP: 2.5 PC: 2.9 ABS: 3.2 SS: 3.0
104°C (220°F) Over, 10 days	Good adherence; slight shrinkage (0%, 3.7%); printing legible; very slight yellowing	Good	Good	PP: 1.4 PC: 2.5 ABS: 2.5 SS: 2.9
121°C (250°F) Over, 10 days	Good adherence; slight shrinkage (2.4%, 5.6%); printing legible; slightly yellowed	Good	Good	PP: 1.2 PC: 2.4 SS: 3.0
149°C (300°F) Over, 10 days	Good adherence; slight shrinkage (5.9%, 4.6%); printing legible; much yellowed	Good	Good	Too brittle for qualitative testing
-40°C Cold Box, 7 hours	Good adherence; no shrinkage; printing legible	Good	Good	Not required
Carbon-arc Weatherometer, 720 hours	Printing very legible; MD Shrinkage: 5.7% CD Shrinkage: 11.9% The sample blistered along top edge, but is intact. One sample cracked in machine direction.	Good	Good	AL: 5.0

*Example 15/16; Substrate: PP=polypropylene; PC=polycarbonate; ABS=acrylonitrile-butadiene-styrene; SS=stainless steel; AL=aluminum

Comparative Example A

Comparative Example A consisted of samples of TESLIN™ Synthetic Printing Sheet, designation SP-800, from PPG Industries. This printing sheet has a thickness of 0.2 mm +/- 0.01 mm (0.008 in, +/- 0.0005 in). Adhesive-coated samples were

5 adhered to panels and subjected to abrasion and fluid immersion tests as reported in Tables 5 and 6.

TABLE 5

	Ink	
	HP 660C Printer HP 51629A Ink	HP 1200C Printer HP 51640A Ink
Ink Dry Time	>1 min, <5 min	>5 min
Image Scratch Resistance	Film burnishes; no effect on image	Film burnishes; no effect on image
Image Quality	Good	Good
Taber Abrasion (CS-10 wheels, 500 g, 100 cycles)	Letters are lighter, but still legible	Letters are lighter, but still legible

10

TABLE 6

Fluid Immersion*	HP 660C Printer HP 51629A Ink		HP 1200C Printer HP 51640A Ink	
	Before Rubbing	After Rubbing	Before Rubbing	After Rubbing
4 hours at Room Temperature				
DI Water	No effect	Image is lighter; still legible	No effect	Image is lighter; still legible
pH 4.0 Solution	No effect	Image is lighter; still legible	No effect	Image is lighter; still legible
pH 10.0 Solution	No effect	Image is lighter; barely legible	No effect	Image is lighter; still legible
Detergent solution	No effect	Image is lighter; barely legible	No effect	Image is lighter; still legible
Isopropanol	No effect	Image is no longer legible	No effect	Image is lighter; still legible

*see Table 3 for fluid compositions

The methods and articles of the present invention can be advantageously used to make durable labels. Such durable labels can be used to display the following types of information: bar codes; information about chemical contents; price; property identification; inventory identification; model number and serial number of an article
5 (so-called "rating plates"); warranty information; and wiring diagrams. It may be desirable to place these types of information in a durable way on the following: appliances; communications equipment; computers, including peripheral equipment and accessories; electronics; industrial products and parts; retail products; automobiles; and goods or packages being transported or shipped. The above examples of printed
10 information and applications are meant to be illustrative and not limiting.

The present invention has now been described with reference to several embodiments thereof. The foregoing detailed description and examples have been given for clarity of understanding only. No unnecessary limitations are to be
15 understood therefrom. It will be apparent to those skilled in the art that many changes can be made in the embodiments described without departing from the scope of the invention. Thus, the scope of the present invention should not be limited to the exact details and structures described herein, but rather by the structures described by the language of the claims, and the equivalents of those structures.

20

WHAT IS CLAIMED IS:

1. An ink jet printable medium, comprising:
a microporous ethylene vinyl alcohol copolymer film having a first major surface and a second major surface.
- 5 2. The ink jet printable medium of claim 1, wherein said microporous ethylene vinyl alcohol copolymer film has a pore volume of at least 25 nL/mm².
3. The ink jet printable medium of claim 2, wherein said microporous
10 ethylene vinyl alcohol copolymer film has a pore volume of from 25 to 300 nL/mm².
4. The ink jet printable medium of claim 1, wherein said microporous ethylene vinyl alcohol copolymer film comprises a maximum limiting pore diameter of at least 0.1 micrometers.
- 15 5. The ink jet printable medium of claim 4, wherein said microporous ethylene vinyl alcohol copolymer film comprises a maximum limiting pore diameter of at least 0.4 micrometers.
- 20 6. The ink jet printable medium of claim 1, wherein said microporous ethylene vinyl alcohol copolymer film is from 0.04 to 0.15 mm thick.
7. The ink jet printable medium of claim 1, further comprising a layer of adhesive provided on said second major surface of said film.
- 25 8. The ink jet printable medium of claim 7, further comprising a release liner provided on the exposed surface of said layer of pressure sensitive adhesive.
9. A method of ink jet printing an image onto the medium of any of claims
30 1-8, comprising the steps of:

a) directing a plurality of droplets of ink towards the recording medium, wherein the recording material comprises a microporous ethylene vinyl alcohol copolymer film;

b) contacting the ink droplets on a first surface of the microporous ethylene vinyl alcohol copolymer film so as to impart a desired image on the first surface; and

c) absorbing the ink into the pores of the microporous ethylene vinyl alcohol copolymer film.

10. The method of claim 9, wherein the ink comprises a plurality of pigment particles suspended in a fluid carrier, and wherein step c) comprises absorbing the particles into the pores of the microporous ethylene vinyl alcohol copolymer film.

11. The method of claim 9, wherein the microporous ethylene vinyl alcohol copolymer film has a sufficient pore volume to absorb all of the ink directed towards the film.

12. The method of claim 10, wherein the microporous ethylene vinyl alcohol copolymer film has a maximum limiting pore diameter sufficient to absorb the pigment particles.

20

13. The method of claim 10, comprising the further step of:
d) subsequent to step c), providing an adhesive on the second surface of the microporous ethylene vinyl alcohol copolymer film.

14. The method of claim 13, comprising the further step of:
e) providing a release liner on the exposed surface of the pressure sensitive adhesive.

15. The method of claim 9, comprising the further step of:
a') prior to step a), providing an adhesive on the second surface of the microporous ethylene vinyl alcohol copolymer film.

30

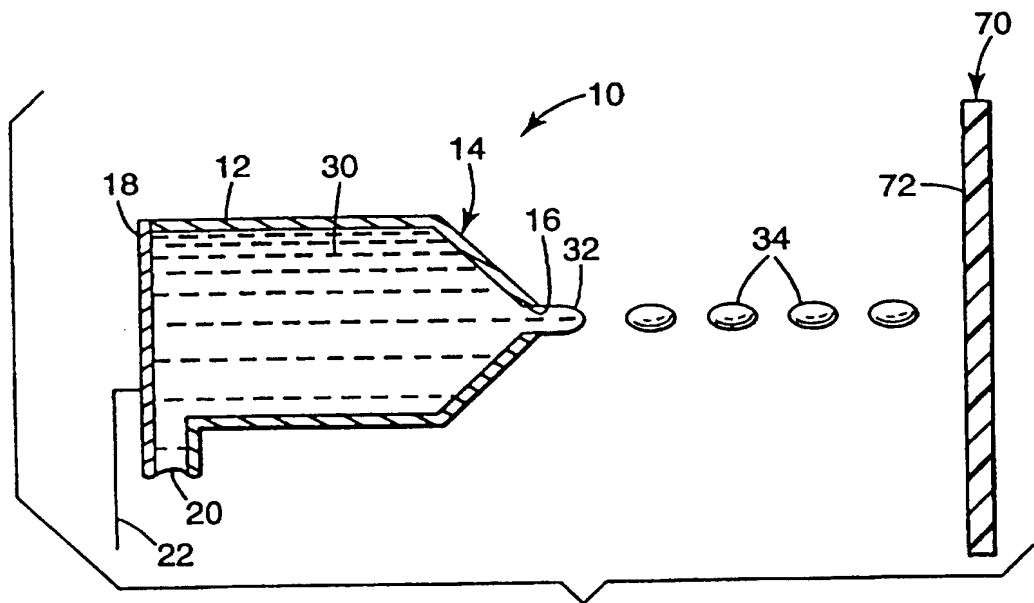
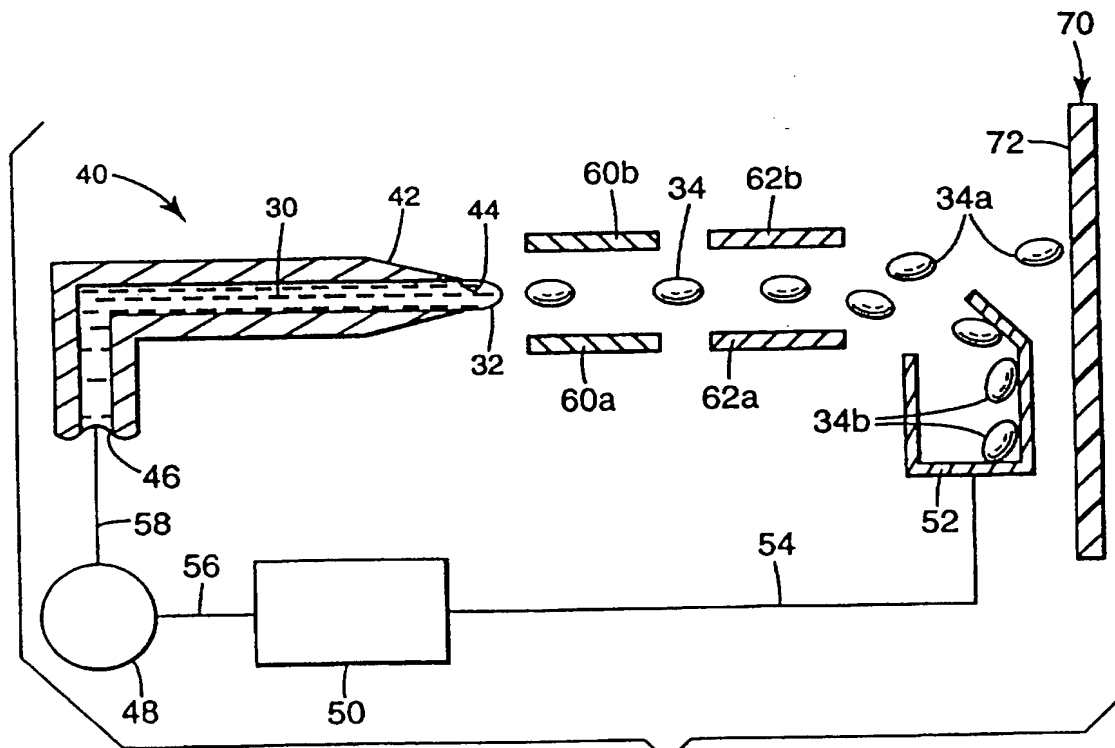
16. The method of claim 15, wherein the adhesive is a pressure sensitive adhesive, and wherein step a') further includes providing a release liner on the exposed surface of the pressure sensitive adhesive.

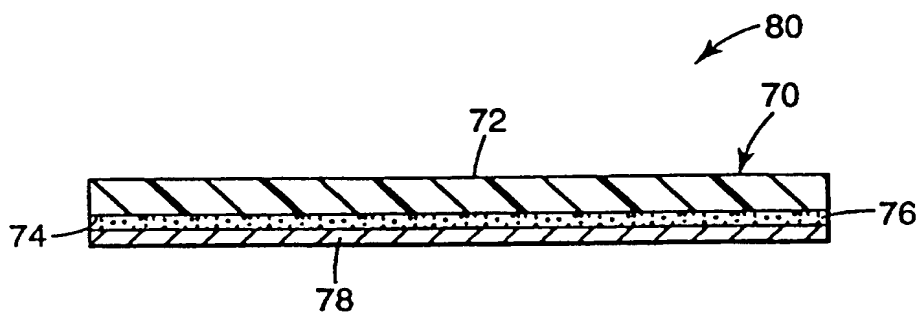
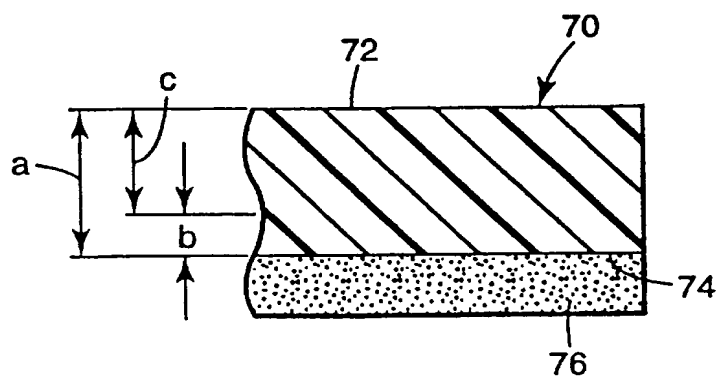
5

17. The method of claim 9, wherein the image is dry to the touch within one minute after printing.

18. The method of claim 17, wherein the image is dry to the touch
10 substantially immediately after printing.

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**Fig. 1****Fig. 2**

**Fig. 3****Fig. 4**

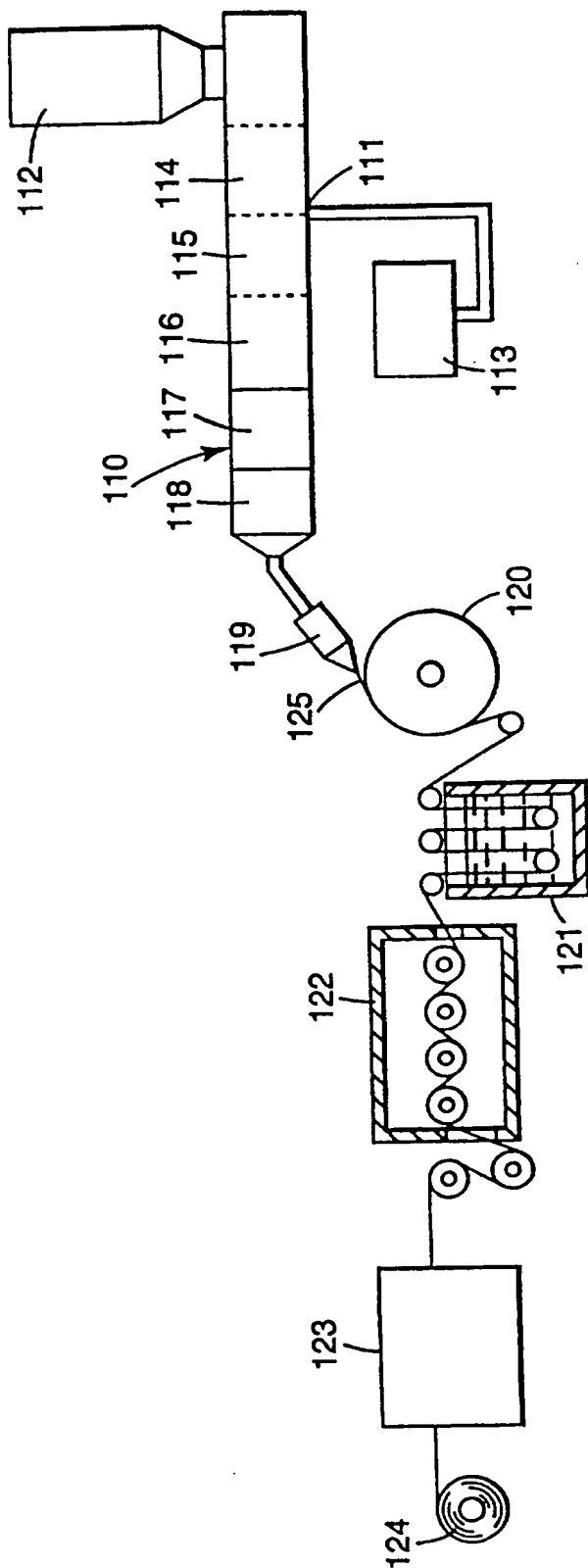


Fig. 5

INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 96/19462

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00 C08J9/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B41M C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 23888 A (UNIV MANCHESTER ;TALLENTIRE ALAN (GB); SINCLAIR COLIN SAMUEL (GB)) 8 September 1995 see the whole document ---	1-6
X	US 4 499 211 A (WALCH AXEL ET AL) 12 February 1985 see the whole document ---	1-6
X	PATENT ABSTRACTS OF JAPAN vol. 95, no. 012 & JP 07 316977 A (KURARAY CO LTD), 5 December 1995, see abstract --- -/--	1-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- * "E" earlier document but published on or after the international filing date
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- * "O" document referring to an oral disclosure, use, exhibition or other means
- * "P" document published prior to the international filing date but later than the priority date claimed

- * "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- * "&" document member of the same patent family

Date of the actual completion of the international search

28 February 1997

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Markham, R

INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 96/19462

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 017, no. 622 (C-1130), 17 November 1993 & JP 05 192222 A (KOKI BUSSAN KK), 3 August 1993, see abstract	1-6
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P,X	WO 96 06184 A (STERIS CORP) 29 February 1996 see page 4, line 12 - line 16 see page 4, line 35 - page 5, line 8 -----	1-6

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Information on patent family members

International Application No

PCT/US 96/19462

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